

Introduction: Estimating the amount of water in the interior of terrestrial planets has tremendous implications on our understanding of solar nebula evolution, planet formation and geological history, and extraterrestrial volcanism. Mars has been a recent focus of such enquiry with complementary datasets from spacecrafts, rovers and martian meteorite studies. In planetary interiors, water can be dissolved in fluids or melts and hydrous phases, but can also be locked as protons attached to structural oxygen in lattice defects in ‘nominally anhydrous’ minerals (NAM) such as olivine, pyroxene, or feldspar [1-3]. Measuring water in Martian meteorite NAM is challenging because the minerals are fragile and riddled with fractures from impact processes that makes them break apart during sample processing. Moreover, curing the sample in epoxy causes problems for the two main water analysis techniques, Fourier transform infrared spectrometry (FTIR) and secondary ionization mass spectrometry (SIMS).

Measurements to date have resulted in a heated debate on how much water the mantle of Mars contains. SIMS studies of NAM [4], amphiboles [5], and apatites [6-8] from Martian meteorites report finding enough water in these phases to infer that the martian mantle is as hydrous as that of the Earth. On the other hand, a SIMS study of glass in olivine melt inclusions from shergottites concludes that the Martian mantle is much drier [9]. The latter interpretation is also supported by the fact that most martian hydrous minerals generally have the relevant sites filled with Cl and F instead of H [10,11]. As for experimental results, martian basalt compositions can be reproduced using water as well as Cl in the parent melts [12,13]. Here FTIR is used to measure water in martian meteorite minerals in order to constrain the origin of the distribution of water in martian meteorite phases.

Method: Mineral fragments are embedded in crystal-bond and doubly polished down to thicknesses of 40-400 μm . After multiple baths in acetone and isopropanol, the samples are analyzed on a Hyperion microscope of a Vertex Bruker FTIR. Transmission FTIR analyses are made in the mid-infrared region with a polarizer and with varying aperture sizes (with sides of 25 to 300 μm and shape adapted to minimize analyzing inclusions and cracks). Water abundances can be calculated using the Beer-Lambert law with the absorbance area beneath the O-H bands, the measured sample thickness and mineral specific absorption coef-

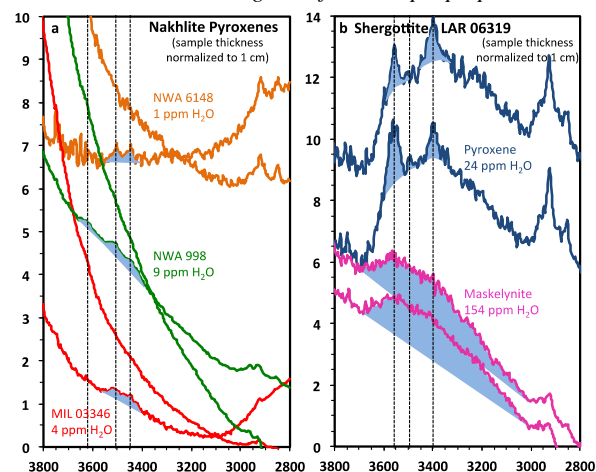
ficients [14-16]. Given that infrared measurements in three mutually perpendicular orientations of an anisotropic mineral relative to the polarizer are necessary for quantification [17], water contents presented here are minimum values because analysis could be done in only two perpendicular orientations in each mineral grain.

Results: *Nakhlites.* No water was detected in an olivine from NWA 998. Spectra of pyroxenes (Fig. 1a) are characterized by small pleochroic OH bands at 3450, 3520 and 3625 cm^{-1} , characteristic of intrinsic H in augite [e.g. 18]. A pyroxene from NWA 998 contains a minimum of 9 ppm H_2O . Three pyroxene grains from MIL 03346 have minimum H_2O contents of 0, 3 and 4 ppm, although the lack of detection of OH bands in one of them may be due to that sample being too thin (75 μm). Three pyroxene grains from NWA 6148 contain 0, 1, and 19 ppm H_2O .

Shergottite LAR 06319. Minimums of 154 and 171 ppm H_2O were measured in two maskelynite grains from a large OH band between 3600 and 3100 cm^{-1} (Fig. 1b). This OH band is not centered around 3200-3300 cm^{-1} like those for typical terrestrial plagioclase [19]. That and the fact that the OH band in maskelynite is not pleochroic may be due to the transformation of the plagioclase into glass during shock. Although no OH bands characteristic of intrinsic water were detected in two olivines from this enriched shergottite, a wide humpback OH band is generally present in the spectra of these quite opaque olivines. Given that the height of this band varies with location on the grain, it may be due to water in melt inclusions that are quite common in this meteorite mm-size olivine phenocrysts [9,20]. Pyroxene grains in LAR 06319 are also characterized by OH bands that are humpback-shaped. However, no melt inclusions have been reported in LAR 06319 pyroxenes [20]. This OH band may be due to a maskelynite contribution despite our best efforts to avoid it when adjusting the FTIR aperture to analyze pyroxene only. One of these pyroxene grains is characterized by additional pleochroic OH peaks at 3560, 3510 and 3400 cm^{-1} which are due to intrinsic H and typical for orthopyroxene (Fig. 1b). The water content from this intrinsic H amounts to 24 ppm H_2O minimum.

Fig. 1: Transmission polarized FTIR spectra in the OH vibration region for nakhlite pyroxenes (a) and shergottite LAR 06319 pyroxene and maskelynite (b) with 2 perpendicular

lar directions of the polarizer relative to each mineral. Bands $<3000\text{ cm}^{-1}$ are due to organics from sample preparation.



Origin of the water in martian minerals: The pyroxene water abundances measured in this study are 100 times lower than those found in most terrestrial pyroxenes. Those for maskelynite are in the same order as those of terrestrial volcanic plagioclases, and most olivine pheno- and xenocrysts from Earth basalts contain $< 5\text{ ppm H}_2\text{O}$ [3,19]. Three main parameters could have influenced these martian water contents.

Shock during impact. No shock experiments have been reported for olivine, pyroxene or feldspar to examine if H disturbance could occur. Nakhilites are the least shocked of all martian meteorites [21] and there is hope that shock has not disturbed the initial water contents. Shergottites, however, have sustained high shock pressures (up to 35 GPa for LAR 06319) and H shock disturbance may have occurred.

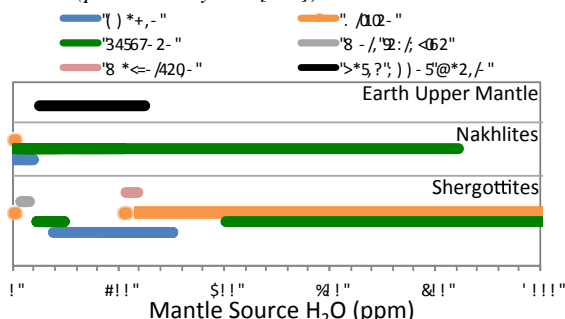
Degassing. Hydrogen is highly mobile at magmatic temperatures and there is evidence that water loss has occurred during magma ascent in terrestrial basalts and their xenoliths [22,23]. My data at this point does not contain any evidence for or against H diffusion in martian minerals.

Magmatic history. Nakhilites are clinopyroxenites thought to represent the cumulate part of thick lava flows [21] with NWA 998 coming from the bottom and MIL 03346 and NWA 6148 the top of the pile [24-26]. NWA 6148 was the fastest to crystallize as testified by the major element zoning of its pyroxenes, then MIL 03346 and finally NWA 998 that has undergone expansive sub-solidus re-equilibration and post-solidus magma circulation. Pyroxene water contents do not correlate either with position in the nakhla pile or cooling rates.

Water abundance of the martian mantle: The water content of the mantle source can be calculated from the data on minerals, using experimentally determined mineral/melt partition coefficients and esti-

mated degrees of crystallization and melting. This exercise is fraught with uncertainties and assumes no water loss through shock and degassing. Calculations from my data give mantle source water contents lower to similar to those of Earth's upper mantle (50-250 ppm H_2O ; [3,27]). When adding the most recent data from the literature, however, estimates of martian mantle water contents vary widely (Fig. 2).

Fig. 2: Estimates of mantle source water contents calculated from measured water contents in martian meteorite minerals (present study and [6-9]).



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